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Attn: 8(d) HEALTH & SAFETY STUDY REPORTING RULE (REPORTING)

Dear Sir or Madam:

As required by 40 CFR 716, as amended, we herewith submit a copy of the following recently completed health and safety study.

Study on the fate of 2,6-TDI (T-0) in eater. Project FE-E-63-III.

Chemical Name

CAS Number

2,6-Toluenediisocyanate

91-08-7

The International Isocyanate Institute (III) project identification number, **FE-E-63-III**, has been marked as part of the title of this report. Please refer to this III identification number in any communication regarding this study. **The enclosed report does not contain any Confidential Business Information.**

This study is sponsored by the International Isocyanate Institute on behalf of the following:

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BASF Corporation
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Very truly yours,


R. K. Rigger
Managing Director

RKR/sha

REPORT

Title

STUDY ON THE FATE OF 2,6-TDI (T-O)
IN WATER

Author(s)

M. KITANO, Y. YAKABE AND Y. SHIMOYAWA

Contractor

Chemicals Inspection and Testing
Institute, Japan.

Observations

This study is part of a programme (Project FE-E-63) to investigate the interactions of isomers of TDI with water under different conditions. Other reports complement the present one.

A programme of studies (FE-E-74) on the interactions of MDI with water is also in progress.

Further information may be obtained from the Scientific Office.

III Project

FE-E-63-III

III File Number

10862

93.01.25

Date of III issue



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Summary

The fate of 2,6-TDI (T-0) in water was investigated under two conditions, vigorous stirring and static conditions, and the results were compared with those of T-100 and T-80.

The following results were obtained:

- (1) Under vigorous stirring condition,
TDI disappeared completely after 24 hours, but the disappearance rate of TDI was slightly slower than T-100 and T-80.
The amount of TDA (2,6-TDA) produced was two times that of T-100 (2,4-TDA).
DOC of test solution at the end of test was nearly the same as T-100 and T-80 and 59.1 % of DOC value was TDA for T-0.
Water insoluble product was not soluble in any organic solvents tested and then the molecular weight of it could not be determined.
- (2) Under static condition,
2,6-TDI (T-0) disappeared linearly like 2,4-TDI (T-100), but the disappearance rate of 2,6-TDI was slower by a factor of more than fifteen than 2,4-TDI. 43.4 % of TDI remained after 91 days.
The amount of TDA produced increased gradually until the end of test. It was about one half of that for T-100 and T-80.

FE-E-63-III

原本

10862

Final Report

FE-E-63 Part III

Study on the fate of 2,6-TDI (T-0) in water

July 31, 1991

Prepared by

Masaru Mitano, Yoshikuni Yakabe and Yuko Shimogawa

Chemical Biotesting Center
Chemicals Inspection & Testing Institute, Japan

Chemical Biotesting Center
Chemicals Inspection &
Testing Institute, Japan

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Far East Environmental Sub Committee

Title of the test

FE-E-63 Part III
Study on the fate of 2,6-TDI (T-0) in water

Test period

October 29, 1990 ~ May 23, 1991

Test personnel

Study director

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5-6-21, Kameido Koto-ku Tokyo 136, Japan

Study staff

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Summary

The fate of tolylene 2,6-diisocyanate (2,6-TDI, T-0) in water was studied under two conditions, vigorous stirring and static conditions, and the result was compared with those of Part I and II of FE-E-63.

Under the vigorous stirring condition, TDI disappeared slightly slower and the amount of the corresponding amine produced was about two times larger than T-100 and T-80.

On the other hand, the disappearance rate of TDI under static condition was slow largely compared with T-100 and T-80 and even after 3 month, about 40 % of TDI remained.

In this study, the variation in the kinetic behavior of the fate of TDI in water with isomer was clarified.

1. Title of research project

Study on the fate of 2,6-TDI (T-0) in water

2. Introduction

In Part I and II of FE-E-63, we studied the fate of 2,4-TDI and mixture of 2,4- and 2,6-TDI (80/20 V/V) in water, respectively, under two conditions; vigorous stirring and static conditions. It was found that the disappearance rate of TDI and the amount of corresponding amine produced were different between the test substance under both conditions. These results suggest that the disappearance rate of TDI and the amount of the amine produced in water are dependent on chemical structure of TDI. Consequently to clarify the variation in these kinetic parameter with isomer of TDI is important in the study on the fate of TDI in environment.

In this report, we studied the fate of 2,6-TDI in water under the same condition as Part I and II of FE-E-63 and the result was compared with those of previous two studies.

3. Purpose of the research

To compare reaction of T-0 in water with that of T-100 and T-80 under vigorous stirring condition.

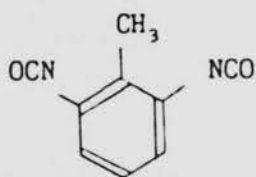
4. Test materials

4.1 Test substance

T-0 (tolylene-2,6-diisocyanate)

(1) Structure

Structural formula



2,6-TDI

Molecular formula $C_9H_6N_2O_2$

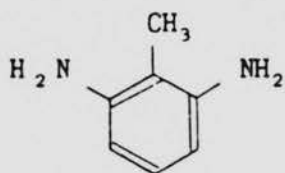
Molecular weight 174.16

4.2 Reference compound

2,6-diaminotoluene

(1) Structure

Structural formula



Molecular formula C₇H₁₀N₂

Molecular weight 122.17

(2) Purity

98 %

(3) Purchase

Purchased from Tokyo Kasei Kogyo Co., Ltd.

5. Test method

The reaction of T-0 with water were examined under two conditions.

5.1 Vigorous stirring system

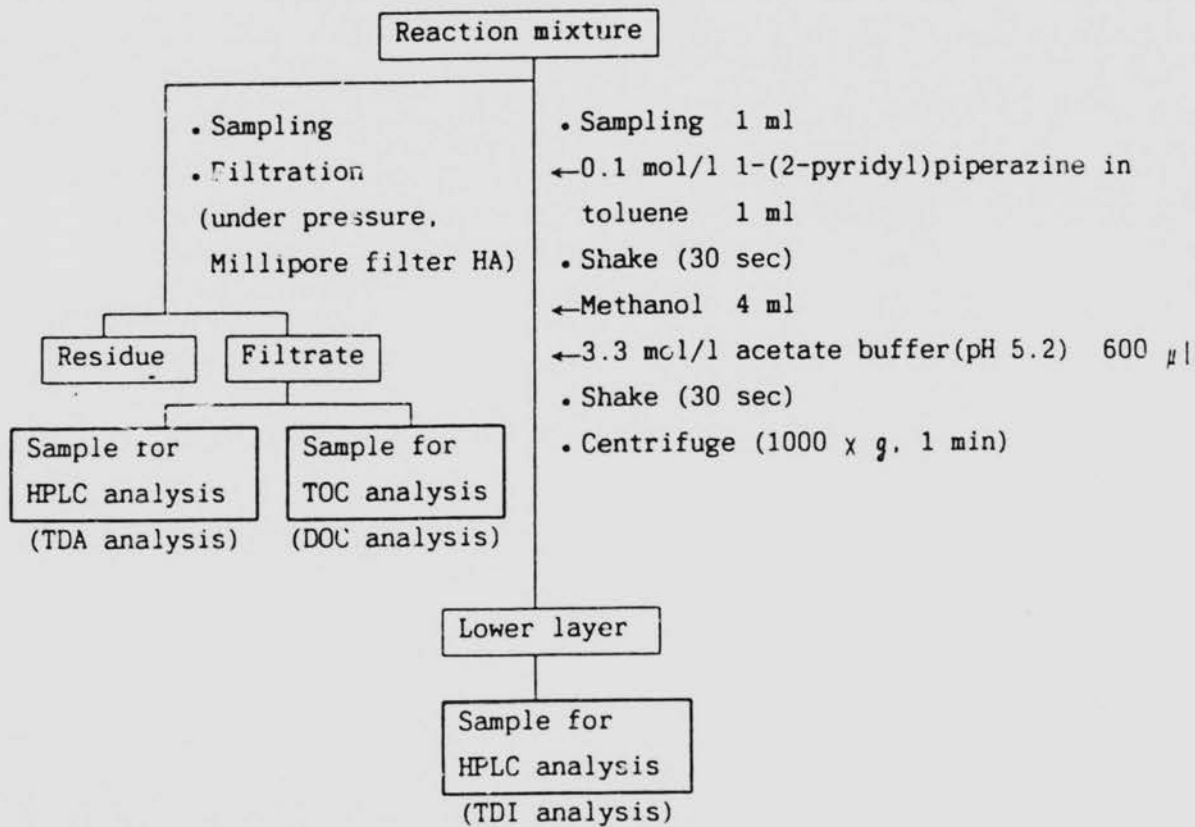
5.1.1 Reaction conditions

Test substance	: T-0 (2,6-TDI)
Nominal concentration	: 1000 mg/l
Water temperature	: 27 ± 1 °C
Water	: Purified water
Addition of TDI	: 250 mg of (specific gravity $1.22 \times 204.9 \mu\text{l}$ = 250 mg) TDI was added into 250 ml of water in a flask (volume of 300 ml) by use of micro pipette.
Mixing apparatus	Magnetic stirrer (IWAKI GLASS Co., Ltd. type PC-351) Teflon stirring bar 4 cm \times 12 mm ϕ Rotation rate 1300 rpm

5.1.2 Pretreatment of analytical sample

Aliquots of reaction mixture were taken out at 0.5, 1, 3, 8 and 24 hours after addition of T-0, and was pretreated to prepare the samples for quantification of residual TDI, TDA, dissolved organic carbon (DOC) according to the flow scheme in the next page.

[Flow scheme]



5.1.3 Analytical conditions

All samples pretreated as described in 5.1.2 were analysed with HPLC and TOC analyzer under following conditions.

(1) Analysis of TDI

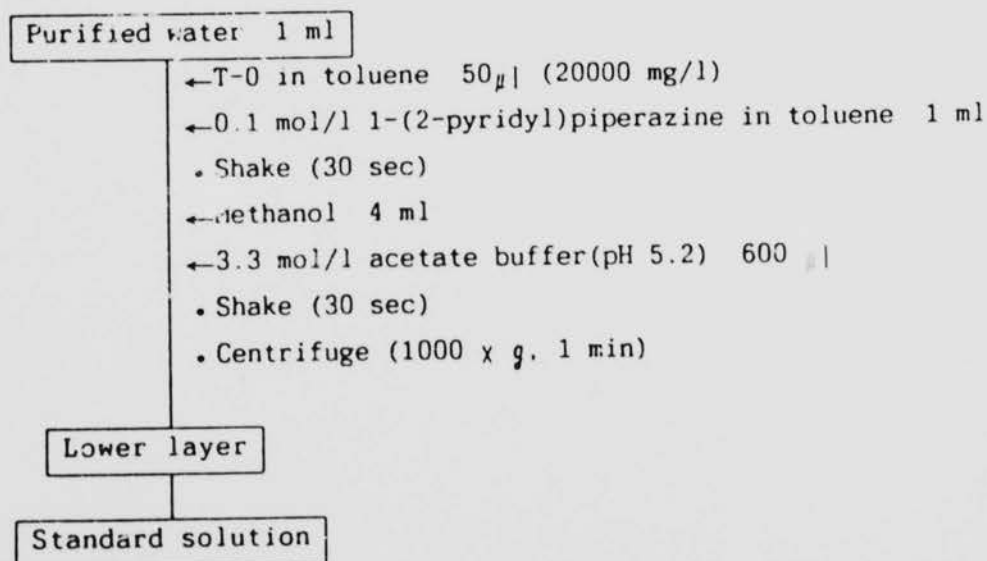
① Analytical conditions

Instrument	High performance liquid chromatograph
Column	Inertsil ODS-2 (Gasukuro Kogyo Inc.) 5 cm x 8 mm ϕ , stainless steel
Eluent	Acetonitrile/0.1mol/l acetate buffer (3/7 V/V)
Flow rate	2 ml/min
Detection wave length	247 nm
Injection volume	6 μ l

② Preparation of standard solutions

Standard solutions were prepared according to the flow scheme.

[Flow scheme]



(2) Analysis of TDA

① Analytical conditions

Instrument	High performance liquid chromatograph
Column	UNISIL Q CN (Gasukuro Kogyo Inc.) 10 cm x 4.6 mm ϕ , stainless steel
Eluent	2m mol/l TBA ^{*1} and 5m mol/l phosphate buffer (pH 7.5) solution
Flow rate	1 ml/min
Detection wavelength	284 nm
Injection volume	10 μ l

1 tetra-n-butylammonium bromide

② Preparation of standard solution

Standard solutions of 1000 mg/l for 2,6-TDA were made by dissolving 100 mg of the samples in 100 ml of purified water and diluted with purified water to concentrations of 20 mg/l 2,6-TDA.

(3) Analysis of DOC

Instrument	Shimadzu total organic carbon analyzer TOC-500
Temperature of furnace	680 $^{\circ}$ C
Carrier gas	air
Flow rate	150 ml/min
Injection volume	10 μ l

5.2 Static system

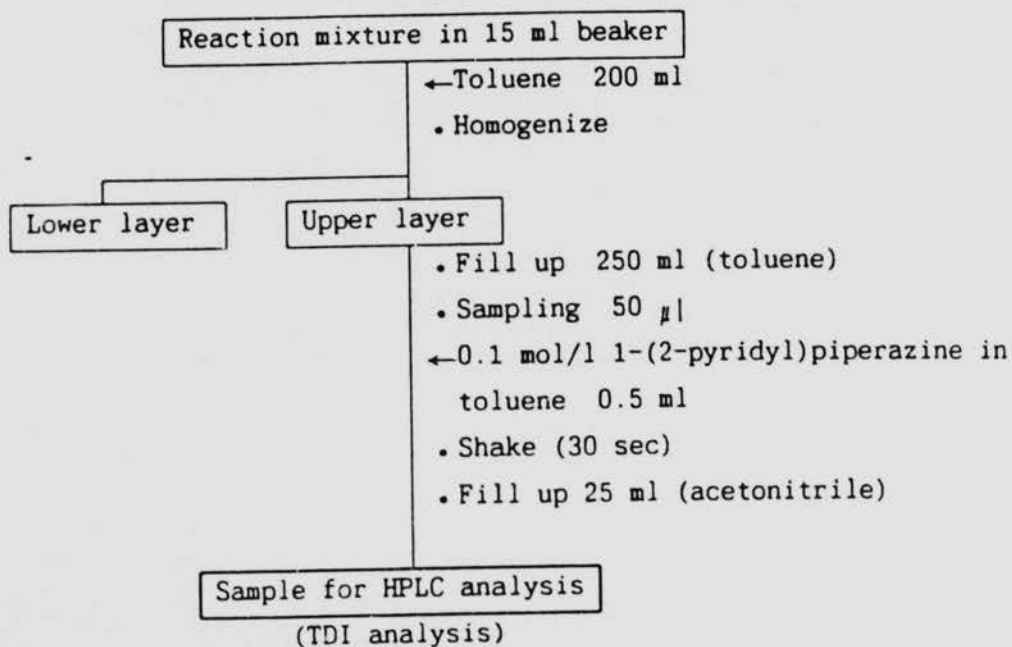
5.2.1 Reaction condition

Test substance	: T-0 (2,6-TDI)
Water temperature	: 27 ± 1 °C
Water	: Purified water
Test procedure	: Three 15 ml beakers were placed on the bottom of one liter beaker which had been already filled with water, then each 5 g TDI (density $1.22 \times 4.1 \text{ ml} = 5 \text{ g}$) was putted slowly avoiding turbulence on the bottom of each three small beakers with measuring pipette, and was kept in a thermostat.
Vessel	: One liter beaker
Apparatus	: Thermostat

5.2.2 Pretreatment of analytical sample

15 ml beakers were taken out from the one liter beaker and the reaction mixtures in them were pretreated by following scheme for quantification of the residual TDI.

[Flow scheme]



5.2.3 Analytical condition

The amount of the residual TDI in the pretreated sample was determined as follows.

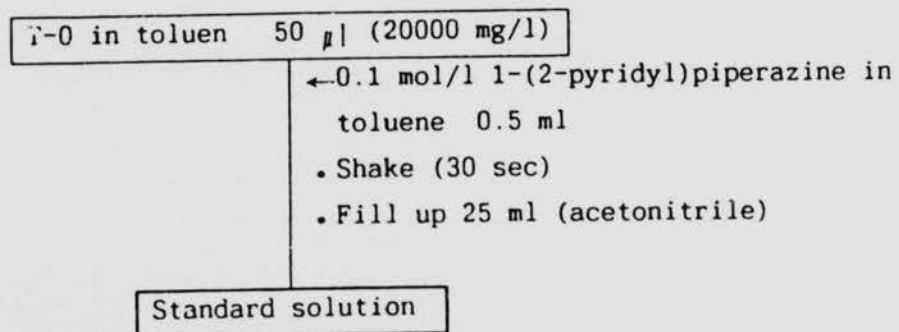
(1) Analytical conditions

The same as in 5.1.3 (1) ①.

(2) Preparation of standard solutions

Standard solutions were prepared according to the following flow scheme.

[Flow scheme]



6. Results

6.1 Vigorous stirring system

6.1.1 Residue of TDI

TDI disappeared rapidly after addition to water under the vigorous stirring condition and after 24 hours it disappeared completely.

Figure 1 shows the time-course of residual TDI for T-0 together with those for T-100 and T-80. There is the tendency that the disappearance rate of TDI increase slightly in order of T-100 > T-80 > T-0.

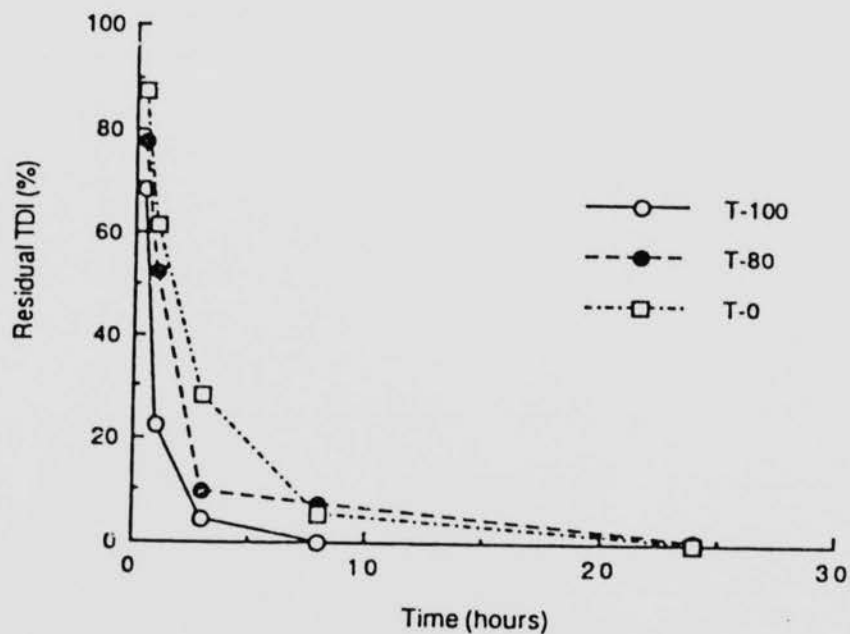


Figure 1. Residual TDI in purified water
[Comparison of TDIs (T-100, T-80 and T-0)]

6.1.2 Concentration of TDA

TDA of 28.8 mg/L was detected after 0.5 hour of test and it increased gradually. Figure 2 shows the time-course of TDA production for three test substances. More than 80 % of final amount of TDA was produced within 0.5 hour for three test substances. Final amount of TDA for T-0 was two times those for T-100 and T-80, but percent production of TDA for 2,4-TDA and 2,6-TDA in T-80 were the same as T-100 and T-0, respectively (Figure 3).

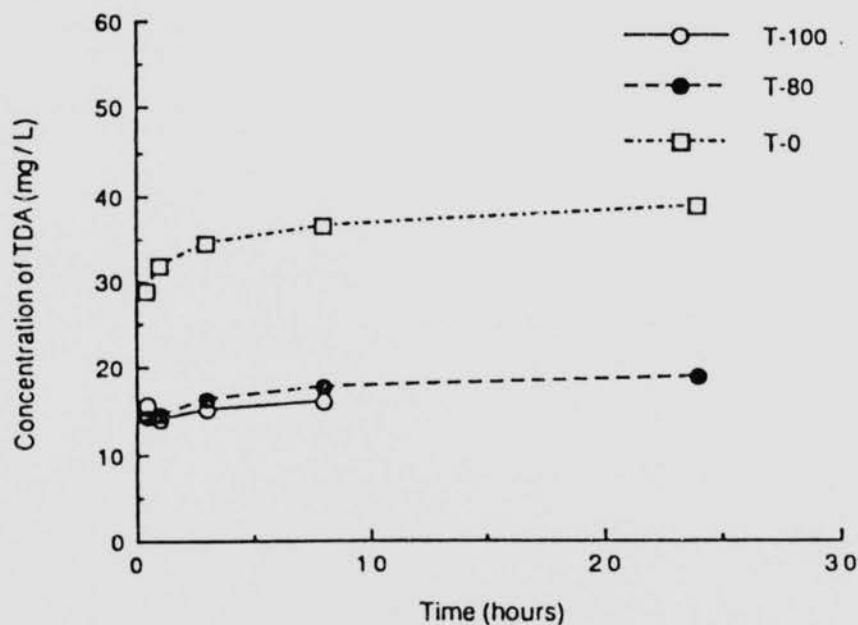


Figure 2. Concentration of TDA in purified water
[Comparison of TDIs (T-100, T-80 and T-0)]

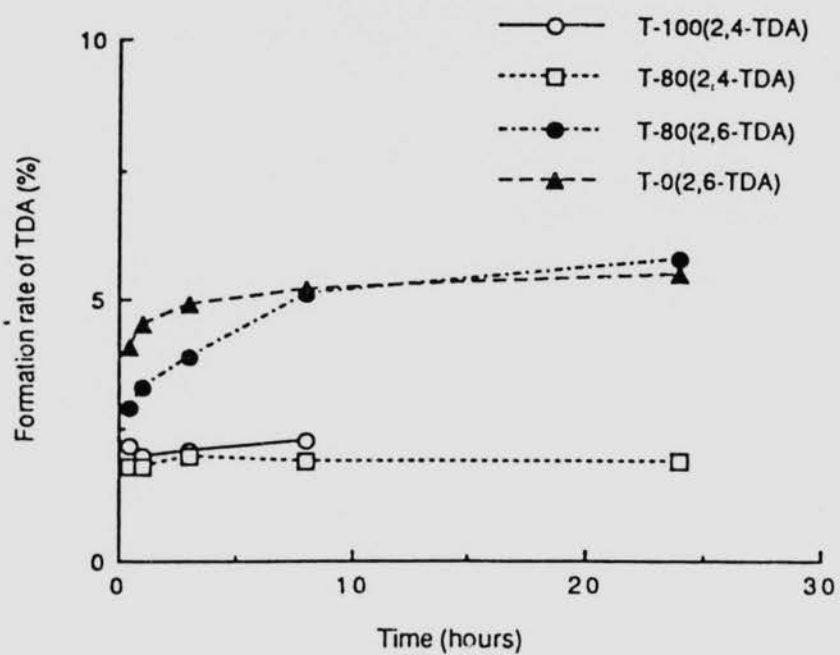


Figure 3. Formation rate of TDA isomers
[Comparison of TDAs (2,4-TDA, 2,6-TDA)]

6.1.3 Concentration of dissolved organic carbon (DOC)

DOC value of test solution was 51.2 mg/L after 0.5 hour and increased slightly after 1 day, followed by gradual decreasing. It was higher than T-100 and T-80 during whole test period (Figure 4). From Figure 2 and 4, 59.1 % of DOC at the end of test was attributed to TDA for T-0, while the contribution of TDA to LOC was 28.2 % and 32.8 % for T-100 and T-80, respectively.

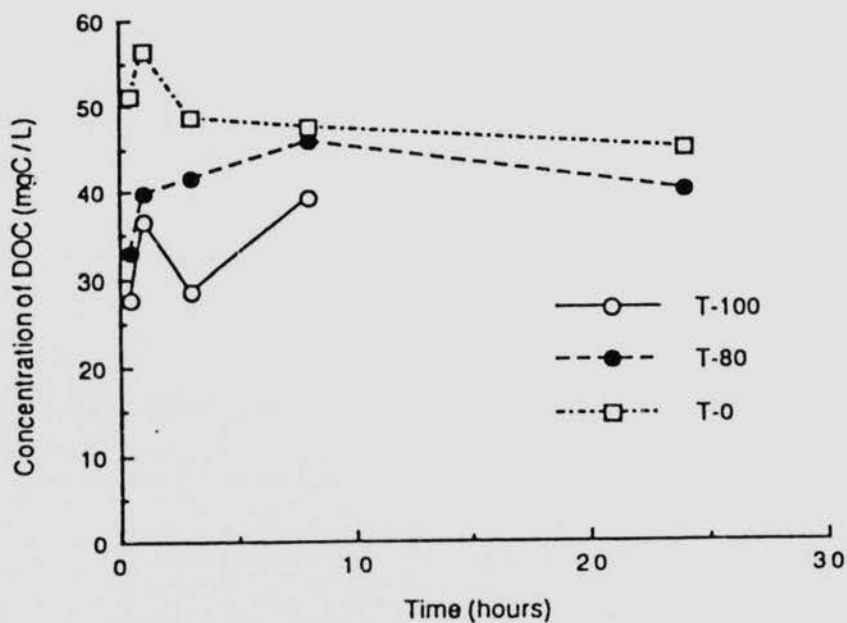


Figure 4. Concentration of DOC [Comparison of TDIs (T-100, T-80 and T-0)]

6.1.4 Peak of retention time 5 min

The peak of the reaction products other than TDA was observed at the retention time of 5 minutes under the condition of 5.1.3 (2)①.

The peak height of this peak is shown below.

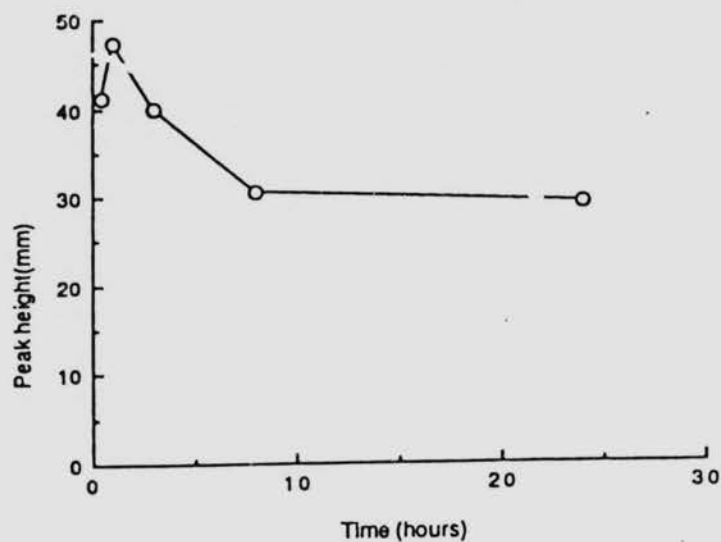


Figure 5-1. Peak of retention time 5 min

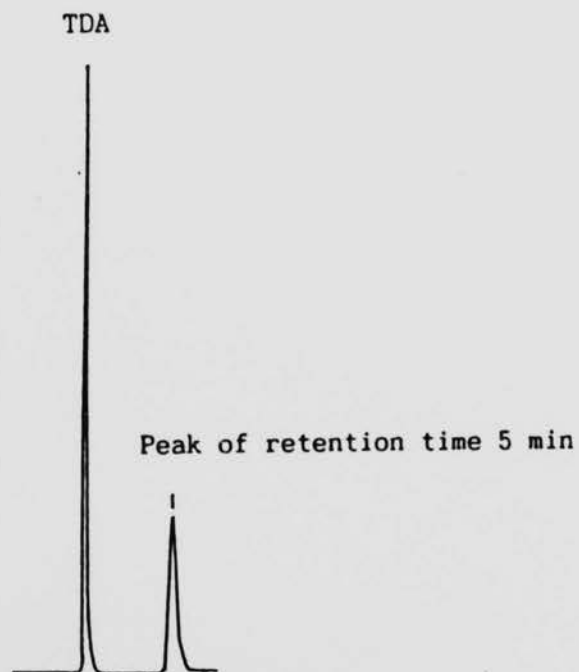


Figure 5-2. Chromatogram of the reaction products

6.1.5 Water-insoluble reaction product

The solubility of water-insoluble reaction product to the following solvents was examined, but it was insoluble to all solvents examined. Accordingly it was impossible to determine the molecular weight distribution of it by HPLC.

Solvents for solubility test

- N,N-Dimethylformamide containing 10m mol/l LiCl
- N,N-Dimethylformamide
- Dimethylsulfoxide
- N,N-Dimethylacetamide
- Hexamethyltriamide Phosphate
- Tetrahydrofuran
- Chloroform
- Hexane
- Acetonitrile
- m-Cresol

6.2 Static system

6.2.1 Residue of TDI

Under static condition, the disappearance rate of TDI was largely slow compared with T-100 and T-80 and then the test was continued for three months. 43.4 % of TDI, however, remained even after 91 days.

Figure 6 shows the variation of residual TDI for three test substances under static condition. The disappearance curve of TDI (2,6-TDI) for T-0 was seemingly linear with time like T-100 (2,4-TDI), but the disappearance rate was slower by a factor of more for T-0 than fifteen than for T-100.

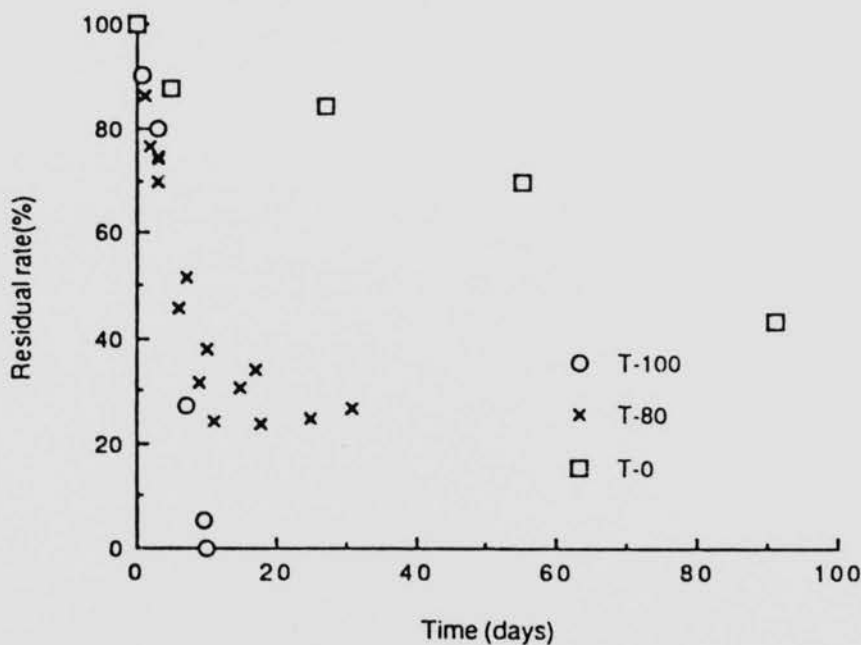


Figure 6. Comparison of residual rate of TDI samples (T-100, T-80 and T-0) under static condition

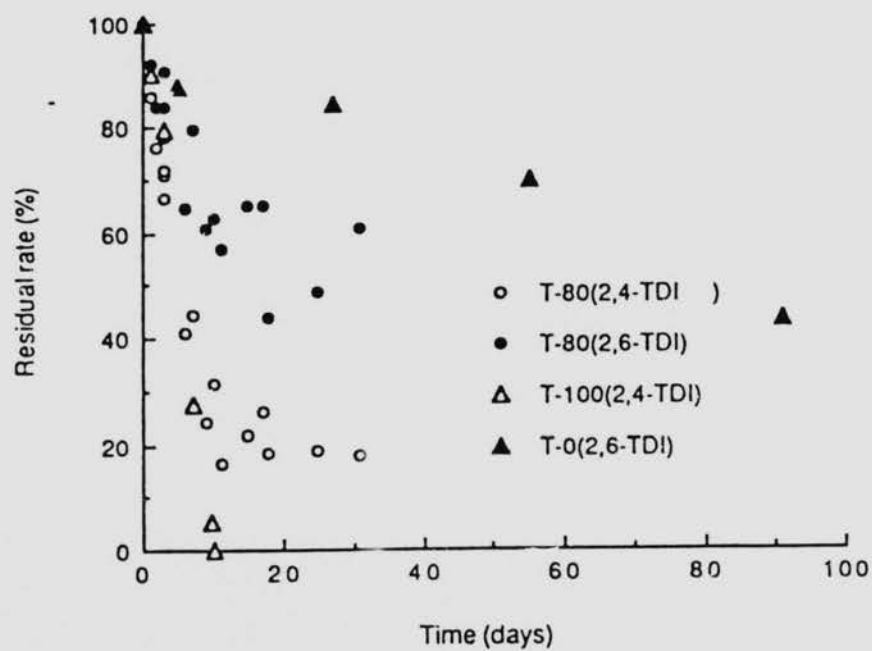


Figure 7. Comparison of residual rate of TDI isomers (2,4-TDI, 2,6-TDI) under static condition

6.2:2 Concentration of TDA

TDA of 3.7 mg/L was detected after 5 days and increased gradually to 9.4 mg/L at the end of test. These values of TDA was about one-half of those of T-100 and T-80, though there was the tendency to increase even at the end of test.

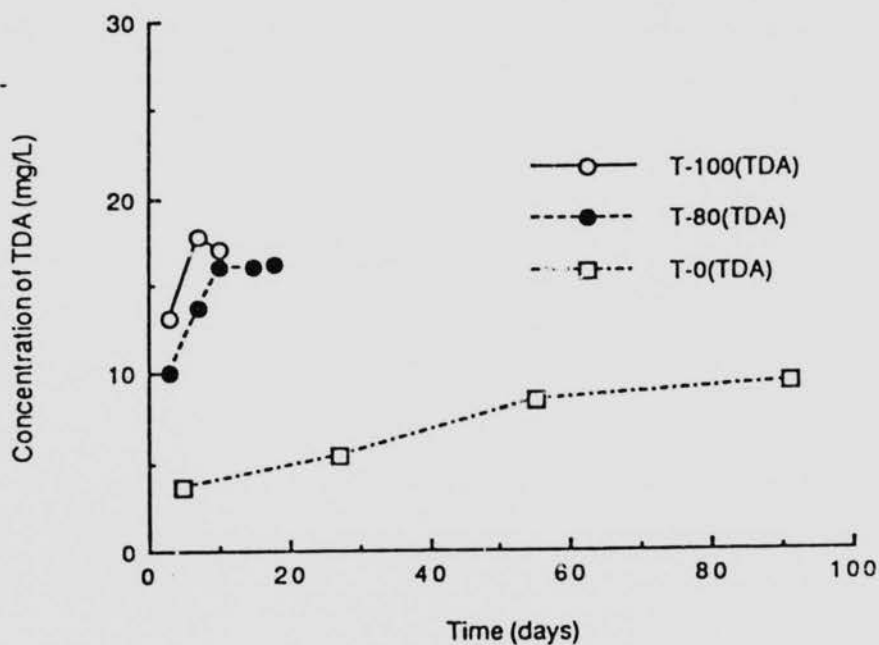


Figure 8. Concentration of TDA under static condition
[Comparison of TDIs (T-100, T-80 and T-0)]

7. Conclusion

The fate of 2,6-TDI (T-0) in water was investigated under two conditions, vigorous stirring and static conditions, and the results were compared with those of T-100 and T-80.

The following results were obtained:

(1) Under vigorous stirring condition,

TDI disappeared completely after 24 hours, but the disappearance rate of TDI was slightly slower than T-100 and T-80.

The amount of TDA (2,6-TDA) produced was two times that of T-100 (2,4-TDA).

DOC of test solution at the end of test was nearly the same as T-100 and T-80 and 59.1 % of DOC value was TDA for T-0.

Water insoluble product was not soluble in any organic solvents tested and then the molecular weight of it could not be determined.

(2) Under static condition,

2,6-TDI (T-0) disappeared linearly like 2,4-TDI (T-100), but the disappearance rate of 2,6-TDI was slower by a factor of more than fifteen than 2,4-TDI. 43.4 % of TDI remained after 91 days.

The amount of TDA produced increased gradually until the end of test. It was about one half of that for T-100 and T-80.

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